

1920
K84

W. G. Koupal

The Corrosive Action
of Illinois Waters

THE CORROSIVE ACTION
OF ILLINOIS WATERS

BY

WALTER GEORGE KOUPAL

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

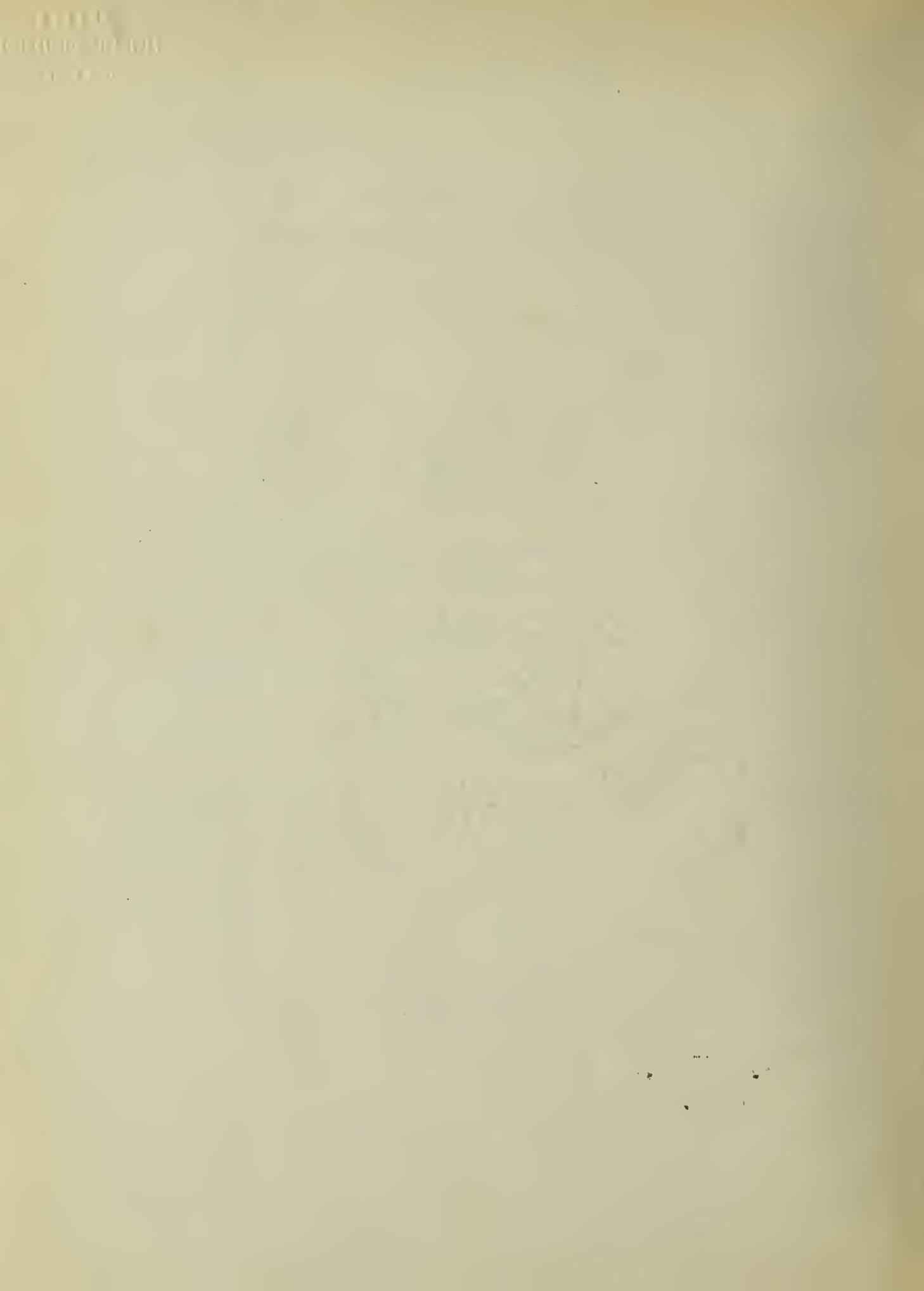
IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1920



1920
KS4

UNIVERSITY OF ILLINOIS

May 10th 1918

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

WALTER GEORGE KOUPAI

ENTITLED THE CORROSIVE ACTION OF ILLINOIS WATERS

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN CHEMISTRY

D. J. McFarland

Instructor in Charge

APPROVED:

W. A. Noyes

HEAD OF DEPARTMENT OF CHEMISTRY

465978



ACKNOWLEDGMENT

The writer wishes to express his sincere thanks to Dr. D.F.McFarland who read the manuscript; and also to Prof. Edward Bartow and Mr. W.F.Monfort under whose direction this work was carried on and to whom the writer is indebted for much valuable assistance.

TABLE OF CONTENTS

	Page
I. Introduction	1
II. Historical and Theoretical	4
Part I	4
Part II	4
Part III	8
III. Experimental	10
Part I	10
Part II	12
Part III	14
IV. Summary and Conclusions	18
Bibliography	20
Acknowledgment	



Digitized by the Internet Archive
in 2013

<http://archive.org/details/corrosiveaction00koup>

I. INTRODUCTION

The corrosion problem is one which has attracted a great deal of attention; especially within recent years when the advance of Industry has necessitated the development of the use of the metals and their alloys and has placed upon them ever increasing demands for durability. The phases of the corrosion problem are as many and varied as are the natural conditions of earth, atmosphere and water, not to mention the great number of what might be called artificial conditions existent in the Industrial world.

This work includes a short selective study of acid resisting alloys, a study of the corrosive action on iron of sulfates in neutral or alkaline solutions, and an examination of boiler concentrates from boilers using a feed water containing sodium carbonate, with a view to determining the presence of formates.

The examination of acid resisting alloys was undertaken at the suggestion of the Director of the Illinois State Water Survey in an effort to find a suitable alloy which could be used in pumps and liners used for the hoisting of waters from Illinois coal mines. These waters often contain considerable quantities of free sulfuric acid formed by the oxidation of iron pyrites occurring with the coal. The work was carried on with special references to a water from the sump of a coal mine at Spring Valley, Illinois. This water, for a period, had been extremely corrosive; it being found necessary to renew the liners at intervals of a week or less. Some time later, a drift of limestone was apparently encountered for the analysis of the water showed a great increase in calcium and magnesium content and a slight alkalinity. Samples of various acid resisting alloys, which promised to be applicable to this use,

were obtained and tested with water synthesized from the analyses of the acid and alkaline water from this source.

1 Within recent years there have been more frequently occurring instances where it has been found necessary and even desirable to use waters from streams containing mine drainage, or water from deserted shafts or sumps. These waters are, as a rule, highly mineralized and contain large amounts of sulfates which are not removed by the methods of treatment for neutralizing and softening which are now commonly used.

2

Various observations have been made of the peculiar corrosive properties of comparatively soft waters containing large amounts of sulfates. Corrosion by these waters causes great losses in leakage from mains and there is always the possibility of contamination of the water supply, especially in the case of suction mains. It was suggested to the writer that this corrosive action might be due to an oxidizing action of the sulfates and this work was carried out with a view to determining whether sulfates could be considered as a potential source of oxygen in the corrosion of iron.

It has been observed for some time that certain condensed waters from pressure boilers were very corrosive to the tubes in the economizers and superheaters. This was generally supposed to be due to the presence of carbonic acid from the dissolved carbon dioxide in the feed waters. A recent work by J.H.

3

Paul has suggested that organic compounds, which he thought to be formates,

1. Neuman. Minn. & Eng. World 45, 985.
Campbell - Coal Age 8, 874.
2. Clark and Gage - Eng. Rec. 65, 545
Campbell - Eng. News 72, 255.
Friend and Barnett - Chem. Trade Jour. 56, 435.
W.S.P. 293 pp. 558-562.
Jones - Eng. & Min. Jour. 64, 368.
Friend - Corrosion of Iron and Steel - p. 36.
Friend & Barnett - Jour. Iron & Steel Inst. 91, 1915.
3. Paul - Boiler Chemistry & Feed Water Supplies.

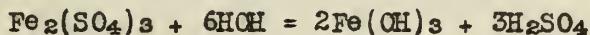
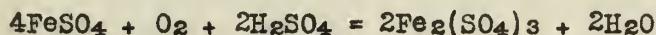
were formed in boilers using a feed water containing sodium carbonate. He states that this corrosion by the condensates is effected by organic acids, part of which at least is formic acid. As the drift in Illinois furnishes a water containing sodium carbonate, water from a number of boilers were examined for the presence of formates.

II. HISTORICAL AND THEORETICAL.

Part 1.

4

The source of the acid which is characteristic of coal mine waters of Illinois has been understood for some time. These waters contain considerable quantities of "free" acid in the form of sulfuric acid and also considerable "reserve" acidity in the form of sulfates of iron and aluminium. This acid is derived from the iron pyrites which occur with the coal. Upon exposure to the air the sulfides are oxidized to sulphates which hydrolyze to give free sulfuric acid and the hydroxide of iron. This oxidation may be represented by the following equations.



Unless there is an adjacent stratum of limestone to neutralize the free acid, these mine waters are very corrosive. Various kinds of piping and liners have been tried but with no great degree of success. Very recently some new alloys especially the high silicon alloys have been developed to meet the demand for acid resisting materials. Samples of a number of these alloys were obtained and treated with synthesized mine waters to determine their applicability for that purpose.

5

Part II.

There have been a number of theories advanced as to the cause of the corrosion of iron by water. Some of these have been generally discarded, but others have been stoutly supported by some individuals while rejected by others.

4. W.S.P. 293 pp. 558-562.

5. L.J.W. Jones. Eng. & Mining Journal 64, 368.

Mining & Eng. World 42, 513.

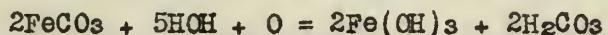
The various theories are:

I. Simple Oxide Theory.

At an early period, the process of rusting was regarded as an ideal example of simple oxidation.⁶ This theory was soon discarded, however, by the discovery of the fact that liquid water was essential to corrosion as well as air or oxygen.

II. The Acid Theory.

The originator of this theory is generally admitted to be Crace Calvert.⁷ The acid theory, or, as it is more commonly, though perhaps incorrectly called, the carbonic acid theory, states that pure water and oxygen are not sufficient to effect corrosion, but that at least a trace of acid must be present. This theory has been the cause of a great deal of controversy and was, until quite recently, the theory most generally upheld. The general reaction may be expressed by the following equation:



The cycle represented here for the carbonic acid may be carried out by any other acid as well, but because of the presence of carbon dioxide in the atmosphere, carbonic acid has been most generally considered. These reactions first expressed by Calvert have been very ably defended by Friend and Moody in recent years; both of these men concluding, as a result of very careful experiments, that pure iron cannot rust in the presence of pure water and oxygen alone.⁸ Lambert and Thompson⁹ from the results of experiments with most ingen-

6. Friend - The Corrosion of Iron and Steel - p.34.

7. Friend - Chemical News 103, 138.

8. Corrosion of Iron & Steel.

9. Proc. Chem. Soc. 1906, 22, 101.

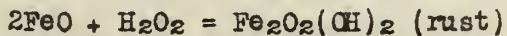
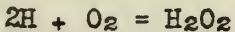
10. Trans. Chem. Soc. 1910, 97, 2426.

ious apparatus have come to the same conclusion. Opposed to this is the work
 11 12
 of Dunstan, Jewett and Goulding and Whitney who conclude from a long series
 of careful experiments that the presence of an acid is not essential. The first
 three of these men, have suggested another explanation which is expressed in
 the:

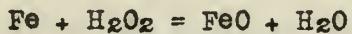
III. Hydrogen Peroxide Theory.

13

This theory was first promulgated by Traube in 1885 and states that
 hydrogen peroxide is formed as an intermediate product in accordance with the
 following equations:-



The excess H_2O_2 then attacks the free iron:-



The inhibitive action of alkalies and chromic acid is explained by their
 ability to decompose the H_2O_2 . Some confirmation also seemed to be gained from
 the fact that delicate tests for H_2O_2 had been obtained in the oxidation of zinc
 14
 and other metals. This theory has been criticized, however, and it has been
 pointed out that although alkalies and chromic acid may decompose, they would
 15
 not prevent the formation of H_2O_2 and no test even with the most delicate re-
 agents, has revealed the presence of H_2O_2 in the rusting of iron. Moreover with
 the above explanation, all strong oxidizing agents should possess an inhibitory
 character, which is not the case.

16

The theory now most generally accepted is the one sponsored by Whitney.

- 11. Trans. Chem. Soc. 1905, 87, 1548.
- 12. Jour. Am. Chem. Soc. 1903, 25, 394.
- 13. Ber. 18, 1881.
- 14. Divers - Proc. Chem. Soc. 21, 251.
Moody - Jour. Chem. Soc. 89, 90, 720.
- 15. Cushman - Corrosion & Preservation of Iron & Steel - p. ⁴⁰.
- 16. Whitney - J.A.C.S. 25, 394-406.

IV. The Electrolytic Theory.

This theory is in accord with the modern theory of solutions and assumes that before iron can oxidize in the wet way it must first pass into solution as a ferrous ion. Water is assumed to be an electrolyte which ionizes thus:



When a strip of pure iron is suspended in pure water a small amount will dissolve passing into solution as Fe^{++} ions and an equivalent amount of H^+ ions will loose their charge and be deposited as a gaseous film on the surface of the metal. Virtually, a solution of $\text{Fe}(\text{OH})_2$ is obtained, but equilibrium is very soon set up unless there is some means of oxidizing and precipitating the $\text{Fe}(\text{OH})_2$ and allowing more iron to come into solution.

It is not hard to reconcile Friends' contention, that at least a minute quantity of acid must be present in the solution, with the electrolytic theory because according to the dissociation theory, even the purest water contains free hydrogen ions to the extent of about 1 gram in 10,000,000 liters and to that extent it is an acid.

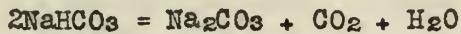
It is generally conceded that oxygen is essential for the corrosion of iron and when the dissolved oxygen in the water proves insufficient, it seems very probable that oxygen containing salts such as sulfates would be a source of the necessary oxygen. The sulfates upon complete reduction to sulfides would unite with the iron setting up potential differences which would further promote corrosion. Recent experiments by Clark brought him to the conclusion that sulfates were reduced to the sulfide. The work of the writer, while confirming the reduction of sulfates, leaves some doubt as to the demonstration of a reduction to sulfide.

17. Cushman - Corrosion & Pres. Fe & Steel - p.41.

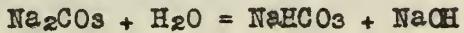
18. Clark, F.R. Thesis 1919.

Part III.

In natural waters containing carbonates of calcium, magnesium and sodium, these salts are present as the bicarbonate or acid carbonates and are entirely soluble. It was formerly assumed that when these waters were used for boiler purposes the bicarbonate was converted merely to the normal carbonate:



¹⁹
The results of more recent work have indicated a further decomposition to caustic soda:



²⁰
From more recent work it appears that in boilers working below 100 lbs. pressure, this conversion to caustic soda is not great, but as the pressure rises, the conversion is more pronounced and at 200 lbs. pressure it is quite marked. It is further pointed out that if the reaction took place according to the equations given, the liberated carbon dioxide must accumulate to the point of saturation in the condensed water, in the case of condensing engines. A gallon of water at normal temperatures will dissolve about 4500 cc. of CO_2 but the examination of several hundred samples of condensed water did not show over 100 cc. of CO_2 per gallon and in most cases this figure was high. The argument that the CO_2 being a gas escapes with the air from the "condensing cycle" does not seem to hold for two reasons:

1. The condensed water is always found to be nearly saturated with free oxygen which is much less soluble in water than carbonic acid.
2. Carbon Dioxide, up to the point of saturation, (4500 cc. per gallon) forms a chemical compound (H_2CO_3) with water which is not readily decomposed

19. Parr - Bull. No. 94, Eng. Exp. Sta. University of Illinois.
20. Paul, J.H. - Boiler Chemistry and Feed Water Supplies.

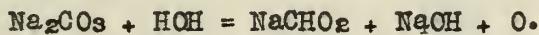
below the saturation point.

From this, four facts appear for consideration:

1. The destruction, partial or total, of the carbonate of soda.
2. The disappearance, partial or total of the CO_2 .
3. The appearance of caustic soda.
4. The constant presence of oxygen in sufficient quantity to keep the condensed water saturated which is remarkable as the steam is condensed in a vacuum.

The presence of free oxygen may be ascribed to the make-up water which may be saturated with oxygen, but the make-up water constitutes only 3% of the condensate which is always saturated and besides there is always an escape of air or gas containing oxygen. It seems more than probable that this excess of oxygen must come from the decomposition of the sodium carbonate.

The appearance of caustic soda and oxygen with the disappearance of carbon dioxide would point to a rearrangement of the molecule of sodium carbonate thus:



This would account for the presence of O_2 and caustic soda as well as the disappearance of the CO_2 . If this reaction has taken place, the carbonate water which originally would not destroy KMnO_4 should do so now as the formates are strong reducing agents. This has been found to be the case, as nearly all boiler waters do reduce KMnO_4 . This has hitherto been ascribed to organic matter present in the original water, but formic acid is an organic acid and part of this reducing power is probably due to formates or condensation products of formates produced in this way.

From this point of view, the highly corrosive action of condensed steam from boilers may be explained by the presence of organic acids and the large amount of dissolved oxygen.

III. EXPERIMENTAL

Part 1.

In carrying out the tests with the various alloys, a quantity of two waters, obtained from the same source as stated above were synthesized. The first according to an analysis obtained from the files of the Illinois State Water Survey and the second according to an analysis made by the writer. The first sample represents the most corrosive mine water that could be obtained. The analyses are given below:

Spring Valley #1

Salt	Grains per U.S. Gallon
NaNO ₃	trace
NaCl	87.6
Na ₂ SO ₄	266.0
MgSO ₄	93.7
CaSO ₄	103.2
MgSO ₄	9.6
FeSO ₄	143.4
Al ₂ (SO ₄) ₃	188.8
H ₂ SO ₄	2.9
	<hr/>
	895.2

Spring Valley #2

NaNO ₃	.20
NaCl	21.42
Na ₂ SO ₄	43.02
(NH ₄) ₂ SO ₄	.62
MgSO ₄	58.50
CaSO ₄	110.50
FeSO ₄	12.79
FeCO ₃	5.49
MnCO ₃	1.17
	<hr/>
	253.71

An effort was made to obtain samples offering the maximum surface area with the minimum weight of specimen in order to remain within the range of the analytical balance. The dressing down of the specimen was rather difficult in

some cases due to the extreme hardness of the alloy. The preliminary dressing was done on a high speed emery wheel and the final dressing was done with finely powdered silica. The specimen was then measured, washed with water, alcohol and ether, dried in an oven, cooled and weighed.

During the treatment, the specimens were immersed in the two waters contained in hard glass beakers set in an empty dessicator to prevent evaporation. Room temperature was maintained for a period of eighteen days.

At the end of that time the specimens were removed, cleaned with finely powdered silica, washed, dried and weighed. At the time of cleaning the specimens, the writer did not know of a suitable chemical which would remove the corroded material and not attack the metal, but owing to the extreme hardness of the alloys, it did not seem probable that cleaning with fine silica would cause appreciable abrasion.

The results are tabulated below:

Alloy	Composition	Loss of weight in Gms. per sq. in.	
		Spring Valley #1	Spring Valley #2
Durion	Silicon - 86% Iron - 14%	.00534	.00383
Hardite "C"	Silicon - Iron	.00829	.00450
"Bario" Metal	Unknown Probably Silicon Iron	.00311	.00091
"Monel" Metal	Nickel - 69% Iron - 1% Copper - 30%	.00474	.00289
Gear Metal "A"	Phosphor Bronze	.00861	.00068
"P.B." Alloy	Phosphor Bronze	.01009	.00046

In no case was there any pitting. The silicon alloys were stained dark in spots but no visible corrosion had taken place. In the case of the bronzes

in the alkaline solution, a reddish film appeared on the surface suggesting that the copper was coming to the surface.

Part II.

The plan for the work on the oxidizing action of sulfates was to treat granulated iron with a sulfate solution in the absence of air and to determine any increase in the sulfur content of the iron. A preliminary examination for sulfur was made on granulated iron prepared by A. Daigger & Co. of Chicago which was supposed to have a sulfur content not to exceed 0.007%. The method of analysis was that used by Clark²¹ in previous work with the same iron and consisted in dissolving the iron in conc. HCl and collecting the evolved H₂S in a standard iodine solution and then titrating the excess iodine with standard Na₂S₂O₃ solution. With this method the writer was unable to obtain check results and the method was given up as unreliable. In order to drive off the last portions of the H₂S it is necessary to heat the solution to boiling. Even with cooling, some of the HCl is carried over and more or less of the iodine is volatilized during the passage of the gases.

²²

Using the ammoniacal cadmium chloride method, however, a number of check results were obtained showing the iron to have sulfur content of 0.118%. To determine the action of the sulfate on iron, one liter of a solution of 4.50 gms. of FeSO₄.7H₂O in boiled distilled water (corresponding to the FeSO₄ concentration of Spring Valley No. 1) was placed in a 2 1/2 liter bottle with 1 gm. of granulated iron, and the air replaced with CO₂. The solution was now shaken in a reciprocating shaking machine for 24 hours. Quite a quantity of the green hydroxide of iron was formed but several attempts showed it to be almost impossible to filter the precipitate of semi-colloidal hydroxide and iron in order to

21. Clark, F.R. Thesis 1919.

22. Treadwell-Hall - vol. 2, p.850.

determine the sulfur content.

This difficulty together with the fact that no iron guaranteed U.S.P. could be obtained induced the writer to proceed in another manner. The procedure outlined above was followed with the exception that an excess of iron (20 gms)
²³ was used and a determination of the sulfate content of the solution was made before treatment and after treatment; the solution being allowed to settle for 24 hours before the final sample was taken for analysis. More satisfactory results were obtained by this method, but it was found that the CO₂ in saturated
²⁴ solution seemed to react with the iron to form a hydroxide and so some nitrogen was prepared and used as an atmosphere. Various concentrations of sulfates were used and other salts were added to determine their effect upon the reaction. The results are tabulated below.

It was suggested that some of the sulfate might be carried down as a basic iron sulfate, but an analysis of the precipitate showed sulfates to be absent.

It was also suggested that the BaCl₂ might be occluding some of the iron present, but blanks run along with the other analyses showed this not to be the case.

A tabulation of the results follows:

23. Treadwell - Hall 2, p.464.

24. Paul - Boiler Chemistry & Feed Water Supplies pp.147-178.

Atmosphere	Composition of solution	Concentration per liter (approx)	Sulfate conc. before treatment (ppts. per m.)	Sulfate conc. after treatment (p.p.m.)	% reduction of sulfate.
CO ₂	FeSO ₄ ·7H ₂ O	4.50	1528.92	1500.16	1.88
CO ₂	FeSO ₄ ·7H ₂ O	4.50	1565.91	1541.25	1.57
Nitrogen	FeSO ₄ ·7H ₂ O	4.50	1602.90	1493.16	6.84
"	FeSO ₄ ·7H ₂ O	4.50	1568.78	1439.73	8.27
"	FeSO ₄ ·7H ₂ O	4.50			
	NaCl	1.50	1570.02	1402.74	10.65
"	FeSO ₄ ·7H ₂ O	4.50			
	NaCl	1.50			
	MgSO ₄ ·7H ₂ O	3.30	2620.13	2480.39	5.33
"	FeSO ₄ ·7H ₂ O	4.50			
	NaCl	1.50			
	MgSO ₄ ·7H ₂ O	3.30	4414.14	4198.36	4.89
"	Na ₂ SO ₄	2.50			
"	Na ₂ SO ₄	6.71	4864.19	4765.54	2.17

It will be noted that the most rapid reduction takes place when an iron salt is in solution in the presence of an electrolyte, and that the reduction is much slower when only a sulfate and the iron are present. Too high a concentration of salts in the solution also seems to have an inhibitory effect upon the corrosion of the iron.

Part III.

In the examination of local boiler waters for the presence of formates, four waters, each from a different source were obtained. The alkalinity of both the raw and boiler water was obtained and the reducing power toward KMnO₄ was observed. As a direct test for formic acid, a 500 cc. portion of the boiler water was neutralized with H₂SO₄ and (Ag)zSO₄ added to precipitate any chloride present. The filtrate was then slightly acidified with H₃PO₄ and distilled over. The first

100 cc. of the distillate was rejected in case it should contain H_2CO_3 and the next 300 cc. of the distillate examined for acid.

The results are tabulated below:

Sample		Alkalinity		Reducing Power c.c. $\frac{N}{20} KMnO_4$	Acidity
		Phenol- phthalein	Methyl orange		
No. 1	Feed water	00 ppm.	374 ppm.		
Boiler pressure 110 lbs.	Boiler water	670 "	1125 "	1.90 cc. per 50 cc. water	---
	Distillate	---	---	---	---
No. 2 Boiler pressure 100 lbs.	Feed water	---	350 "	---	---
	Boiler water	936 "	1446 "	1.30 cc. per 50 cc. water	---
No. 3 Boiler pressure 90-100 lbs.	Distillate	---	---	---	---
	Feed water	---	320 "	---	---
No. 4 Boiler pressure 175-85 lbs.	Boiler water	610 "	950 "	0.90 cc. per 50 cc. water	---
	Distillate	---	---	---	---
No. 4 Boiler pressure 175-85 lbs.	Feed water	---	320 "	---	---
	Boiler water	660 "	960 "	1.00 cc. per 50 cc. water	---
No. 4 Boiler pressure 175-85 lbs.	Distillate	---	---	Reduced small amt. of $KMnO_4$ Middle 300 cc. 1.40 $\frac{N}{20} NaOH$	neutralized

With the exception of No. 4 the presence of formates in the boiler water appears doubtful. The boiler waters do reduce $KMnO_4$, but as no acid was obtained on distillation in the first three cases, this might be attributed to the presence in the feed water of small amounts of organic matter which had been concentrated in the boiler and converted to a form which would reduce $KMnO_4$.

It will be noted, however, that in the case of No. 4 where a $KMnO_4$ reducing acid was obtained, that the boiler pressure was considerably higher than in the other cases.

As no other boiler waters from boilers working at high pressure were available, high pressure boiler conditions were simulated by the use of a small copper-lined autoclave. In the first run a solution of about 3 gms. of Na_2CO_3 per liter of distilled water was used; thus precluding the entrance of any organic matter. The pressure varied from about 90 lbs. to 175 lbs. for a period of 72 hours. The mean temperature was about 180°C .

It was found that 50 cc. of this treated solution when acidified, would reduce about 9.0 cc. of $\frac{N}{20} \text{KMnO}_4$.

A 500 cc. portion of this solution was neutralized with H_2SO_4 and treated with $(\text{Ag})_2\text{SO}_4$, filtered, acidified with H_3PO_4 and distilled.

Separate portions of 15 cc., 85 cc., and 300 cc. respectively were collected. The solution up to that point had a constant boiling temperature of 102°C . The reducing power of the first 15 cc. was tested and it was found to reduce 1.5 cc. of $\frac{N}{20} \text{KMnO}_4$.

50 cc. of the 85 cc. portion neutralized 1.80 cc. of $\frac{N}{20} \text{NaOH}$ and reduced 2.50 cc. of $\frac{N}{20} \text{KMnO}_4$. 100 cc. of the 300 cc. portion neutralized 1.70 cc. of $\frac{N}{20} \text{NaOH}$ and reduced 1.50 cc. of KMnO_4 .

Some of the acidity of the first portions of the distillate might be attributed to carbonic acid, but the reducing power must have been due to the presence of some oxidizable compound and the reducing properties of the acid distilling over after all the H_2CO_3 must have been removed, indicate strongly the presence of formic acid.

Another run using a concentration of about 12 gms. of Na_2CO_3 per liter was made. The pressure was maintained fairly constant at about 200 lbs. with variation, for short periods, of from 23-30 lbs. on either side. The temperature averaged about 195°C . At the end of 72 hours the autoclave was allowed to cool and a 500 cc. portion of the solution was treated as described above and distilled.

The first portions of the distillate had a penetrating odor resembling formic acid or formalin which was strong enough to irritate the passages of the nose and throat. The first 50 cc. neutralized 7.0 cc. of $\frac{N}{20}$ NaOH and reduced 14.0 cc. of $\frac{N}{20}$ KMnO₄. The middle 300 cc. of the distillate neutralized 10 cc. of $\frac{N}{20}$ NaOH and reduced somewhat over 20 cc. of $\frac{N}{20}$ KMnO₄.

These more positive results were what had been expected from the use of higher pressures and greater concentration and they seem to indicate clearly the dissociation of Na₂CO₃ under boiler conditions into other products than caustic alkali and carbon dioxide.

IV. SUMMARY AND CONCLUSIONS

I. Test plates of six alloys were treated with two synthesized mine waters and the corrosion per unit area determined. The results show that each of the metals would be suitable for the purpose as far as corrosion resisting properties indicate, but the cost of the different alloys would be the determining factor.

II. Granulated iron was treated with solutions freed from dissolved oxygen and containing sulfates in varying quantity in the presence and absence of other electrolytes.

The results show that:

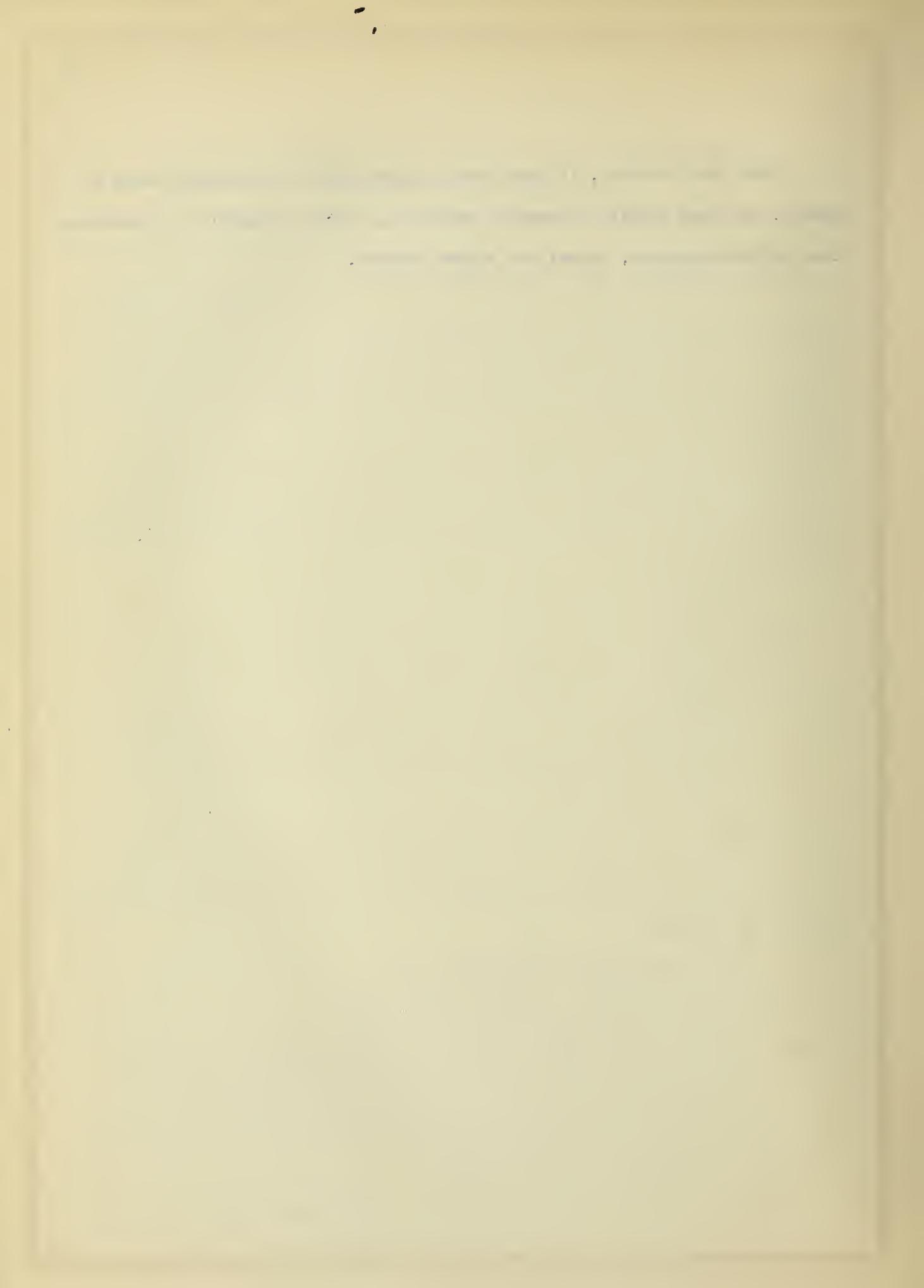
1. Sulfates are a source of oxygen for corrosion, but are potentially so only when free oxygen is absent.
2. The presence of an electrolyte will hasten the reaction, but a high concentration of salts in solution has an inhibitory action.

III. Four boiler waters from boilers using a NaHCO_3 feed water, and solutions of Na_2CO_3 treated with pressure in an autoclave were examined for the presence of formates.

The results of the examination show:

1. The feed waters did not reduce KMnO_4 .
2. The boiler waters and treated Na_2CO_3 solutions all reduced KMnO_4 to a greater or less extent. This reducing power, in the case of the Na_2CO_3 solutions at least, was not due to the presence of organic matter.
3. The high pressure boiler water and the treated Na_2CO_3 solutions contained a volatile acid which reduced KMnO_4 .

From these results, it seems very probable that at pressures above 150 pounds, and more rapidly at greater pressures, sodium carbonate is dissociated into sodium hydroxide, oxygen and sodium formate.



BIBLIOGRAPHY

1. Neuman - Min. & Eng. World 45, 985.
Campbell - Coal Age 8, 874.
2. Clark & Gage - Eng. Rec. 65, 545
Campbell - Eng. News 72, 255.
Friend & Barnett - Chem. Trade Jour. 56, 435.
W. S.P. #293, pp. 558-562.
Jones - Eng. & Min. Jour. 64, 368.
Friend - Corrosion of Iron & Steel, p.36.
Friend & Barnett - Jour. Iron & Steel Inst. 91, 1915.
3. Paul - Boiler Chemistry & Feed Water Supplies.
4. W.S.P. #293, pp. 558-562.
5. L.J.W. Jones - Eng. & Min. Jour. 64, 368.
Min. & Eng. World 42, 513.
6. Friend - The Corrosion of Iron & Steel - p.34.
7. Friend - Chem. News 103, 138.
8. Friend - The Corrosion of Iron & Steel.
9. Moody - Proc. Chem. Soc. 1906, 22, 101
10. Lambert & Thompson - Trans. Chem. Soc. 1910, 97, 2426.
11. Jowett & Goulding - Trans. Chem. Soc. 1905, 87, 1548.
12. Whitney - Jour. Am. Chem. Soc. 1903, 25, 394.
13. Traube - Ber. 18, 1881.
14. Divers - Proc. Chem. Soc. 21, 251.
Moody - Jour. Chem. Soc. 89, 90, 720.
15. Cushman - Corrosion & Preservation of Iron & Steel, p.40.
16. Whitney - Jour. Am. Chem. Soc. 25, 394-406.

17. Cushman - Corrosion & Preservation of Iron & Steel, p.41.
18. Clark, F.R. Thesis 1919.
19. Parr - Bull. No. 94, Eng. Exp. Sta. University of Illinois.
20. Paul, J.H., Boiler Chemistry & Feed Water Supplies.
21. Clark, F.R. Thesis 1919.
22. Treadwell - Hall - Analytical Chemistry 2, p.850.
23. Treadwell - Hall - Analytical Chemistry 2, p.464.
24. Paul, J.H., Boiler Chemistry & Feed Water Supplies pp. 147-178.

UNIVERSITY OF ILLINOIS-URBANA



3 0112 079097876